博士論文（要約）

Electrical transport and optical functionality in two-dimensional crystals of transition-metal dichalcogenides

（遷移金属カルコゲナイド二次元結晶の電気伝導と光機能）

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1, Introduction & Purpose of this work

Two-dimensional crystals (2D crystals) are novel platforms holding two-dimensional carrier gases, namely two-dimensional electron gas (2DEG) and two-dimensional hole gas (2DHG), which are not only playing crucial rules in the present information technology, but also fruitful playgrounds of fundamental physics such as quantum transport and next-generation electronic technologies. 2DEG and 2DHG have been traditionally investigated at interfaces of conventional bulk semiconductors, but those residing in 2D crystals are further beneficial for facility in obtaining high quality systems. 2D crystals represent thin single crystals (typically Å – 100 nm thick) isolated from bulk layered materials, which have highly anisotropic bondings: a strong covalent bonding within each layer and a weak van der Waals bonding between layers. Researches based on 2D crystals are triggered by the successful isolation of graphene on 2004, and have spread to cover various kinds of layered materials. In particular, 2D crystals isolated from transition-metal dichalcogenides (TMDs) are promising candidates both for transistor device application and for investigating novel physics.

TMDs are semiconductors and thus more suitable for transistor device than graphene which has difficulty to realise a highly resistive state owing to the zero-gap band structure. TMDs are inhered by two gaps: indirect ones close to the Γ point and direct ones at ±K points, edges of the hexagonal Brillouin zone. Gap energies and the relative energy difference depend on the thickness of 2D crystals, owing to the varying interlayer interaction. TMD 2D crystals with thickness from bulk down to bilayer are indirect gap semiconductors, while monolayers are direct gap semiconductors owing to the vanishing interlayer interaction, which significantly modifies physical properties, especially optical properties.

The purpose of this research, based on these background, is to investigate electronic transport properties and possible application for opto-electronic devices using TMD 2D crystals, in particular MoS_2, $MoSe_2$, and WSe_2.

2, Experiment

In this research, we selected electric double layer (EDL) for gate dielectrics among various kinds of available insulators for field effect transistors (FETs). EDL is an analogue of nano-gap capacitor formed at the solid/liquid interface, and enables a wide range modulation of channel carrier density in the order of 10^{14} /cm^2. This carrier density is one – two orders in the magnitude higher than those reached within solid gate dielectrics.

Single crystals of TMDs are grown by chemical vapour transport method. TMD 2D crystals were mechanically exfoliated from those crystals and transferred onto highly-doped Si substrate with SiO_2 surface layer. The lateral dimension of our 2D crystals are typically in the order of 1 – 10 μm. Electrical contacts were fabricated by electron-beam lithography and vacuum deposition methods.

Electrical properties were mainly evaluated by low temperature electrical transport measurement under high vacuum and under magnetic field. In addition, polarization-resolved micro-luminescence spectroscopy are combined to low temperature transport measurement, in order to investigate optical functionalities.

3, Electrical transport of TMD 2D crystals

We first checked conventional FET performance of WSe_2 and MoS_2 2D crystals with SiO_2 as gate dielectrics. Clear ambipolar and unipolar (*n*-type) transports were observed for WSe_2 and MoS_2, respectively, in consistent with prior works. The absence of hole (*p*-type) transport in MoS_2 has been attributed to sulphur vacancies leading to an unintentional electron doping. When MoS_2 is gated through EDL, we realised a clear hole transport as large as electron transport, being the first observation of ambipolar behaviour in MoS_2, likely owing to the large carrier density modulation of EDL that can deplete the unintentionally doped electrons in MoS_2.

Electronic states of EDL-gated TMDs are found to show metallic behaviour both under electron- and hole-doping. In addition, superconducting transitions with a drastic drop of resistance were observed in further electron-doped MoS_2. Similar phase transition from insulator to superconductor via metal was also observed in $MoSe_2$ with a slightly lower superconducting transition temperature (T_c), while no signal of superconductivity was recognised for WSe_2, probably owing to the heavier atomic weight. A quasi-continuous sweeping of the carrier density in MoS_2 revealed that the critical electron density for metallic conduction is 6.7×10^{12} /cm^2 and for superconductivity 6.8×10^{13} /cm^2. Additionally, the T_c varies non-monotonically with electron density, forming a dome-like superconducting region in temperature – electron density phase diagram. This is ascribed to the modulation of population ratio between different Fermi pockets (called “valleys”) in the conduction band of electrostatically doped MoS_2. The highest T_cs for MoS_2 and $MoSe_2$ are 10 K and 7 K, respectively, both are larger than those found in chemically doped compounds.

4, Novel optical functionality in TMD 2D crystals

Valley-related phenomenon in TMD 2D crystals

In addition to the modulation of the band structure, monolayer TMDs has unique physical properties. First, the orbital angular momentum of Bloch states representing ±K points, contributed by both the atomic orbital and the phase factor, remains finite and depends on valley (±K), owing to the inversion asymmetric crystal structure of monolayer. Consequently, opposite circularly polarized light is required to optically excite electrons from the valence band to the conduction band at ±K points. This phenomenon is called as valley circular dichroism. Second, a large spin-orbit interaction leads to a valley-dependent spin splitting at ±K points with spins perfectly oriented to out-of-plane direction. These exclusive coupling between optical polarization, valley, and spin is unique to TMDs, in particular, monolayer TMDs, and attracting a number of researchers working on next-generation electronics, such as spintronics and valleytronics, and quantum information processing.

Electroluminescence from TMD 2D crystals

Considering valley or spin as an information carrier, it is required to transfer information recorded as valley or spin polarization into light that are used for telecommunication, and vice versa. With TMDs, those information is expected to be transferred into the circular polarization of light. The fundamental device that realize electrical – optical and optical – electrical conversions is the *p*-*n* junction. We adopted field-effect doping using transistor device structure, instead of general chemical doping, in order to embed a *p*-*n* junction inside a single domain of a TMD 2D crystal, since domain boundaries act as valley scatterers. Effectively setting the gate electrode to zero voltage and applying voltages with opposite signs to the source and the drain electrodes, electrons and holes can be simultaneously induced in the channel TMD 2D crystal, forming a *p-n* junction.

Clear electroluminescence (EL) was observed from all members of TMDs when *p-n* junctions were forward biased. By comparing EL spectra with photoluminescence (PL) and absorption spectra, we found that electrons and holes, which are respectively injected from *n-* and *p*-doped regions, first form excitons and then undergo radiative recombination. Moreover, polarization-resolved luminescence measurements, which can selectively record right- or left-handed circularly polarized component, have revealed that there exist net intensity difference between two components, even without intentional injection of valley polarized carriers into *p-n* junctions. A net circular polarization indicates that strength of EL from K and –K valleys are different. Following the theory of those days, such EL only occurs when valley polarization exist, as is the case for PL excited by circularly polarized laser, but in our measurement condition this mechanism is less likely. It is worth noting that such a circularly polarized EL was not reported from other groups, who were investigating EL from TMD 2D crystals using conventional solid gate dielectrics.

Discussion

As the situation of EL is distinct from PL, we tried to construct an effective model for circularly polarized EL. The degree of circular polarization in EL from TMD 2D crystals reached about 50 % for all compounds we have investigated: MoS_2, $MoSe_2$, and WSe_2. This value is as high as that in PL from MoS_2 and WSe_2, but is one order in the magnitude larger than that from $MoSe_2$. Such a large difference in degrees of polarization suggests a distinct difference in mechanisms of polarized PL and EL.

A clear difference in experimental conditions between PL and EL is the existence of in-plane electric field. In a *p-n* junction, a large in-plane electric field is applied between source and drain electrodes in order to drive electrons and holes into the junction, while PL is usually measured without applying such a bias. This electric field shifts the position of electrons and holes in the momentum space from its equilibrium position, indicating that centres of electron and hole distributions are away from the exact ±K points. Although this electric field may not affect the valley circular dichroism itself because the valley circular dichroism holds for relatively wide regions around ±K points, distribution shifts can affect the radiative recombination probability, which depends on the overlap of electron and hole distributions in the momentum space. Taking into the anisotropic band dispersion and dissimilar mobility and effective mass for electrons and holes, we found that the recombination probability can indeed be different between ±K valleys, which can qualitatively explain the experimental results.

Unique functionality: valley light-emitting transistor

According to the mechanism discussed above, the degree of polarization in EL is seriously affected by the relative orientation between the electric field and the crystal orientation, which determines the direction of the distribution shift and the anisotropy of the band dispersion, respectively. In particular, it is expected to change sign by reversing the direction of the electric field with a fixed crystal orientation. This operation exchange the situation of charge distribution shifts in ±K valleys. Taking the advantage of reversibility in field-effect doping, we switched the doping profile in a single TMD 2D crystal transistor, and recorded EL spectra for each current direction. We found that the sign of the degree of circular polarization indeed changed between two opposite current directions in both WSe_2 and $MoSe_2$ *p-n* junctions. To date, these devices, named as valley light-emitting transistors, are the only devices which can electrically control the polarization, among various kinds of circularly polarized light emitters.

5, Summary

We found that electronic states of TMD 2D crystals changes from insulating to metallic by electrostatically doping either electrons or holes, and further doping of electrons leads to an occurrence of superconductivity, owing to a large carrier density realised by EDL gate dielectrics. The huge carrier accumulation also realises a new functionality, electrically switchable circularly polarized light emission, which is unique to TMD 2D crystals with inherent valley circular dichroism. A qualitative explanation of this phenomenon was constructed by focusing on the charge distribution shifts in the momentum space. Such a functional light emitter has never been achieved with other active materials, and is expected to contribute to a various kinds of technologies, for instance, stereo displays and integrated circuits for quantum computation.